

Capacity of Some California Alkaline Brines for Sulfur Dioxide  
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INTRODUCTION

Following the 1973 fuel crisis, a national movement began to discover economical methods for either removing sulfur directly from coal, or to discover ways of burning the coal without the evolution of harmful, sulfur oxides. A number of proposals have been made for the absorption of sulfur oxides such as the use of sea water or the use of raw Trona ( $\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$ ) taken directly from Wyoming deposits and dissolved in water for the absorption.

California contains scattered natural reserves of highly alkaline brines which could also be used for the absorption of sulfur oxides. These alkaline dry lakes located primarily in desert areas have significant absorption capacities for the sulfur oxides and in addition contain valuable minerals, e.g., boron and tungsten. This report will show that as a result of the brine acidification with  $\text{SO}_2$ , tungsten can be recovered much easier, thus using a potential air pollutant to aid in natural resource recovery.

When high sulfur fuels are burned, two and possibly more acidic gases are produced, viz: carbon dioxide, sulfur dioxide and lesser amounts of sulfur trioxide and nitrogen oxides. As the acidic oxides pass into an alkaline salt solution, they are neutralized forming salts such as sulfite, sulfate, bicarbonate and nitrites. As the gases are absorbed, the pH will continue to decrease in solution. With decreasing pH, some of the less stable weaker acid salts will release their gases such as  $\text{CO}_2$  from solution.

The chemistry of the brines is quite complex since a number of basic salts (carbonate, bicarbonate, borate and metaborate) are present as well as neutral salts such as  $\text{NaCl}$ ,  $\text{KCl}$ , and  $\text{Na}_2\text{SO}_4$ . Because the brines are also quite concentrated (400 g/l), the usual stoichiometry and equilibria applicable in dilute systems do not always apply. In addition, salts such as borate and metaborate contribute a buffering capacity. With such a system, direct experimental measurement is the best approach.

The experiments in this study were performed using a brine from Searles Lake California. The lake is located about 185 miles northeast of Los Angeles and covers about 13 square miles of exposed surface. The salt body covers the whole 13 square miles of surface and a much larger subsurface area to a depth of 50 to 75 feet. During most of the year, the surface of the salt body is dry and hard but in winter after rains liquid may be two or three inches above the top of the salt body (1).

A typical brine analysis from Searles Lake is indicated in Table I (2). The brine contains about 35% dissolved solids. The composition varies somewhat at different locations; the lower structure brine contains more carbonate and borate than does the upper structure brine. It is apparent that this vast natural lake contains a ready sink for the sulfur dioxide.

TABLE I  
TYPICAL BRINE ANALYSES FROM SEARLES LAKE

<u>Constituent</u>	<u>Upper Structure Brine, wt %</u>	<u>Lower Structure Brine, wt %</u>
KCl	4.90	3.50
Na <sub>2</sub> CO <sub>3</sub>	4.75	6.50
NaHCO <sub>3</sub>	0.15	
Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub>	1.58	1.55
Na <sub>2</sub> B <sub>2</sub> O <sub>4</sub>		0.75
Na <sub>2</sub> SO <sub>4</sub>	6.75	6.00
Na <sub>2</sub> S	0.12	0.30
Na <sub>3</sub> AsO <sub>4</sub>	0.05	0.05
Na <sub>3</sub> PO <sub>4</sub>	0.14	0.10
NaCl	16.10	15.50
H <sub>2</sub> O (by difference)	65.46	65.72
WO <sub>3</sub>	0.008	0.005
Br	0.085	0.071
I	0.003	0.002
F	0.002	0.001
Li <sub>2</sub> O	0.018	0.009

#### EXPERIMENTAL

##### Apparatus and Reagents

1. Sulfur dioxide compressed gas containing in percent: 0.47 SO<sub>2</sub>, 33.07 CO<sub>2</sub>, 3.43 CO and the balance (approx. 63%) nitrogen.
2. Flow meter, Fischer and Porter No. 08F 1/16-12-5-36 set for 62 ml per minute gas flow by calibration.
3. Fischer-Milligan gas absorption bottles.
4. Hydrochloric acid (1:99), potassium iodate (0.2225 grams per liter) equivalent to 0.10 mg of sulfur per ml and starch indicator mixed appropriately to monitor sulfur dioxide absorption efficiency.

##### Absorption Train for SO<sub>2</sub> Bearing Gas



- A - Tank of compressed SO<sub>2</sub> bearing gas and regulator.
- B - Flow meter.
- C - Searles Lake brine in Fischer Milligan bottle.
- D - Sodium carbonate indicator solution with phenolphthalein used with 100% SO<sub>2</sub> gas when separating 50 ppm tungsten from 100 ml of brine.
- E - 100 ml tall form beaker and gas bubbler used with 50 ml buret to deliver KIO<sub>3</sub> solution for titration of SO<sub>2</sub>.

#### DISCUSSION OF RESULTS

The data on the absorption of the SO<sub>2</sub> bearing (0.47% SO<sub>2</sub>) combustion gas indicates that about 71 grams of SO<sub>2</sub> can be absorbed per liter of raw Searles Lake brine. The efficiency of the single scrubber was 98% with an aliquot (2.5 ml to 100 ml) of the concentrated brine using the experimental apparatus at a gas flow of 62 ml per minute ( $8.6 \times 10^{-4}$  g of SO<sub>2</sub> per minute). Sulfur dioxide break-through occurred after a total elapsed time of 4 hours and one minute. The net alkaline absorbance time (correcting for water absorbance) was 226 minutes. The break-through was detected by noting the continued fading of the blue iodine starch color from the exit gas bubbled into beaker E.

Because the data of Table I are analyses which can vary with location, the analyses of the actual brine used in the experiments is shown in Table II. It lists the principal sodium salts of the Searles brine and their calculated concentrations based on cation and anion analyses of the raw brine sample used. Not listed is approximately 65 grams per liter of KCL which is the principal potassium salt for a brine of specific gravity 1.30 at 21°C.

TABLE II  
COMPOSITION BY ANALYSIS OF SELECTED COMPONENTS  
OF SEARLES LAKE BRINE

<u>Component</u>	<u>Concentration</u> <u>(g/l)</u>	<u>Calculated As</u>	<u>Concentration</u> <u>As (g/l)</u>
Sodium	149.4		
Potassium	34.8		
Carbonate	35.2	Na <sub>2</sub> CO <sub>3</sub>	62.3
Chloride	151.0	NaCl	249.1
Bicarbonate	5.2	NaHCO <sub>3</sub>	7.2
Sulfate	61.0	Na <sub>2</sub> SO <sub>4</sub>	90.3
Tetraborate	16.8	Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> ·10H <sub>2</sub> O	41.3

The SO<sub>2</sub> absorbing capacity of the selected sodium salts at the given concentration can be seen in the data of Table III for a 2.0 ml aliquot of each salt. The comparison of the total absorption

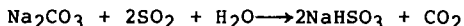
capacity for the sum of the synthetics was 165 minutes versus 168 minutes for a 2.0 ml aliquot of the actual brine with the 0.47% SO<sub>2</sub> combustion gas. This confirms that the synthetic data is giving a true absorption capacity for all the salts tested. Surprisingly even Na<sub>2</sub>SO<sub>4</sub> is contributing slightly. The principal SO<sub>2</sub> absorbers appear to be sodium carbonate (76%) followed by sodium tetraborate (15%), sodium bicarbonate (6%) and sodium sulfate (3%).

Table III  
SULFUR DIOXIDE ABSORPTION CAPACITY OF SELECTED  
SALTS PRESENT IN SEARLES LAKE BRINE - 2.0 ML ALIQUOT

<u>Salt Concentration (g/l)</u>	<u>pH (initial)</u>	<u>pH (after)</u>	<u>Absorbance, Time (min)</u>	<u>Net Absorb. Time (min)</u>
41.3 Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> ·10H <sub>2</sub> O	9.20	3.12	39	24
7.2 NaHCO <sub>3</sub>	7.97	3.35	25	10
62.3 Na <sub>2</sub> CO <sub>3</sub>	11.65	5.45	141	126
90.3 Na <sub>2</sub> SO <sub>4</sub>	8.01	3.10	20	5
Water Blank (100 ml)	6.70	2.98	15	-

Absorbance equals  $8.6 \times 10^{-4}$  grams of SO<sub>2</sub> per minute and net absorbance is corrected for the water blank.

The reserves of sodium carbonate in Searles Lake have been estimated to be in excess of 150 million tons (3). Hence this huge carbonate reserve plus the other alkaline salts could provide a source of alkaline neutralizing capacity for high sulfur coal or oil burning power plants located near Searles Lake or sufficiently close so that the brine could be pumped to the location. In the case of Na<sub>2</sub>CO<sub>3</sub> the reaction with SO<sub>2</sub> follows:



Based on the above equation and assuming complete reaction, a brine of 62.3 g/l Na<sub>2</sub>CO<sub>3</sub> (Table II) should absorb 75.2 grams of SO<sub>2</sub> per liter. However as shown in Table III, only 76% of the absorbing capacity was due to sodium carbonate, i.e., 71 (total SO<sub>2</sub> absorbance) x 0.76 or 54 grams of SO<sub>2</sub> per liter. This implies an efficiency of  $54/75 \times 100$  or 72% if the neutralization were to go completely to NaHSO<sub>3</sub> formation from Na<sub>2</sub>CO<sub>3</sub>. As the data of Table III indicate for pure Na<sub>2</sub>CO<sub>3</sub>, the final pH after SO<sub>2</sub> absorption was 5.45 which lies close to the value observed on SO<sub>2</sub> gassing of the raw Searles brine.

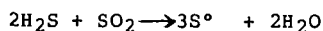
### TUNGSTEN RECOVERY

As indicated earlier, tungsten is one of the more valuable mineral components in Searles Lake brine. Although present at only 50 ppm, the amount of brine in the lake is so great that the total amount of tungsten is estimated at 170 million pounds of  $WO_3$ , equaling the total of all other known U.S. reserves. Earlier workers (4) had indicated that the tungsten might be recovered with organic reagents if the brine could be acidified by carbonating the liquor with flue gas. The data of Table IV indicates that tungsten requires a low pH for recovery from brine. Evidently, the rather weak acid nature of carbonic acid makes  $CO_2$  a poor choice to reduce the pH of alkaline brines. Obviously the borate salts served as a buffer to prevent sufficient  $CO_2$  acidification.

TABLE IV  
RECOVERY OF TUNGSTEN FROM SEARLES LAKE BRINE  
WITH ORGANIC REAGENTS SELECTIVE FOR TUNGSTEN

Test	Pretreatment	Organic Reagent	% W Recovered
1	$SO_2$ to pH 5.5 $H_2SO_4$ to pH 2.0	8-Hydroxyquinoline	0
2	Same as above	Cinchonine	20
3	$CO_2$ to pH 9.0	Tannic acid 8-Hydroxyquinoline	0
4	$SO_2$ to pH 5.5	Tannic acid 8-Hydroxyquinoline	15
5	None	Tannic acid Cinchonine	0
6	$SO_2$ to pH 5.5	Tannic Acid Cinchonine	100

100 ml of brine were used which would yield about 7.0 mg of tungstic oxide ( $WO_3$ ). Also pure  $SO_2$  gas was used rather than the dilute combustion gas (0.47%  $SO_2$ ) so that the acidification could be completed in a reasonable time. Upon  $SO_2$  gassing a yellow precipitate of sulfur first formed in the brine. These studies with pure  $SO_2$  gas contacting the raw brine implies first a possible Claus reaction between the  $SO_2$  and the  $Na_2S$  present (500 ppm) in the raw brine, i.e.,



After completion of the  $SO_2$  gassing, the sulfur precipitate was filtered from the solution, washed, ignited and subject to spectrographic analysis.

The data of Table V show that very little tungsten is removed with the elemental sulfur but that nearly 6% of the residue is arsenic.

TABLE V  
EMISSION SPECTROGRAPHIC<sup>1</sup> ANALYSIS OF SULFUR  
RESIDUE FROM SEARLES LAKE BRINE IGNITED TO OXIDE

<u>Element</u>	<u>Percentage</u>
Na	32.
K	5.7
As	5.8
B	0.24
W	0.12
Cu	0.057
Si	0.23
Ca	0.095
Li	0.0059
Ag	0.00082
Ni	0.0030
Cr	0.054
Fe	0.026
Mo	0.0079
Ti	0.0095

Sulfur residue ignited at 570°C for 1 1/2 hours to produce a gray residue weighing 0.1004 grams separated from 100 ml of brine with SO<sub>2</sub> gas.

<sup>1</sup> This procedure was by arc semiquantitative optical emission.

Following the sulfur filtration, the filtrate was treated by standard methods using the reagents of Table IV. It is evident that high molecular weight reagents (cinchonine 294 and tannic acid 1701) are necessary to precipitate tungsten from a highly saline solution.

The data of Table VI for the ignited tungsten residue were obtained by a semi-quantitative analysis for all elements except tungsten which was analyzed by a modification of the McKaveney (5) hydroquinone photometric procedure. The modification involved fusion of the ignited residue with potassium pyrosulfate followed by a leach with sulfuric acid and dilution to 50 ml. An aliquot was then added to the hydroquinone for color development. The principal impurities in the tungstic acid are sodium and potassium with lesser amounts of silicon, boron and probably occluded chloride and sulfate. A water or dilute nitric acid leach should solubilize most of these impurities out of the tungstic acid.

TABLE VI  
EMISSION SPECTROGRAPHIC ANALYSIS OF IGNITED OXIDE  
RESIDUE FROM TANNIC ACID - CINCHONINE SEPARATION  
OF SO<sub>2</sub> TREATED SEARLES LAKE BRINE

Element	%	Element	%
Na	23.	Ba	0.22
K	5.8	Fe	0.048
W	25.0	Ti	0.084
Ca	0.069	Zr	0.16
Al	0.19	Mo	0.035
Si	1.3	Sn	0.014
B	2.1	Cr	0.064

#### TECHNICAL AND ECONOMIC CONSIDERATIONS

Kerr-McGee, is now expanding its operations at Searles Lake. It is constructing a 64 megawatt coal fired power plant (6). The purpose is to replace scarce natural gas and to supply processing steam and electricity for their chemical operations. The carbon dioxide from coal combustion will be used for brine carbonation to manufacture sodium bicarbonate. By using higher sulfur fuels, SO<sub>2</sub> absorption could be used for easier tungsten recovery while carbon dioxide could be diverted to present chemical operations.

The authors have cited the utility of alkaline brines for the useful application of a harmful pollutant (SO<sub>2</sub>) from coal or oil combustion. Also, their specific application dealt with Searles Lake and some modifications would be necessary for deposits containing other ratios of carbonate, borax and bicarbonate which are present in other California brines. In the future, the use of pipeline transportation of coal in water slurries may make many of these remotely located alkaline deposits realistic for power plant siting. The water from the slurry may be useful for cooling purposes. Also, the use of pipelines for transportation of seawater to inland locations may make it possible to utilize excess power plant heat for flash distillation of needed water. Seawater is relatively dilute in salt compared to the salt content of the dry lake or subsurface brine waters.

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